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Three-dimensional (3D) arrays of silicon nanosize elements in the void sublattice of artificial opals

V. N. Bogomolov†, N. A. Feoktistov†, V. G. Golubev†, J. L. Hutchison‡, *D. A. Kurdyukov*†, A. B. Pevtsov†, J. Sloan‡ and L. M. Sorokin†

† Ioffe Physico-Technical Institute, St Petersburg, Russia

‡ Department of Materials, Oxford University, Parks Road, Oxford OX1 3PH, UK

Abstract. Silicon is now the most important material in modern solid state electronics. Regular systems of silicon nanoclusters containing up to 10^{14} cm^{-3} elements have been fabricated in a sublattice of opal voids. Structural studies of samples by TEM, HREM and Raman measurements were carried out. The regular lattices of Pt-Si junctions were obtained and their current-voltage characteristics (CVC) were investigated.

Introduction

Contemporary solid-state electronics is based on planar technology. Transition to 3D systems of semiconductor devices is necessary for futher increase of the volumetric density of elements. By using 3D dielectric matrices similar to opal, it may be possible to obtain three-dimensional ensembles of semiconductor nanodevices with density of elements as high as 10^{14} cm^{-3}.

1 Experimental

To fabricate semiconductor nanocomposites we used 'monocrystals' of synthetic opals having optically perfect structure [1]. The opals consist of 250 nm diameter close packed amorphous silica spheres and have regular sublattice of voids (45–90 nm) up to 26% accessible to filling by other substances [2].

To incorporate silicon into opal samples the thermal CVD technique was used [3]. The CVD-reactor consisted of a quartz tube with an external heater, through which a gas mixture of SiH_4 (5%) and Ar was passed. An opal plate was placed perpendicularly to gas flow. The reactor design excluded of a gas flow around a sample. As a result of silane thermal decomposition a silicon film was deposited on the inner surface of opal cavities. The conditions of decomposition were isothermal.

To increase the volume fraction of nanocrystalline silicon phase the samples were annealed at $T = 800$°C and pressure about 1 Torr.

The silicon structure was determined by TEM, HREM and Raman measurements. Electron microscopes JEM4000EXII and JEM2010EX equipped with EDX attachment for element analysis in the object region with size 3–5 nm were used. The microstructure images both in diffraction contrast and high resolution modes were taken.

The sample intended for structure analyses was grinded on abrasive paper with the grain size 5 μm up to thickness 70–80 μm. Plates with the linear sizes no more than 3 mm (diameter of a sample holder) were cut out. Further thinning was carried out by Ar^+-ion milling up to thickness, transparent for electrons.

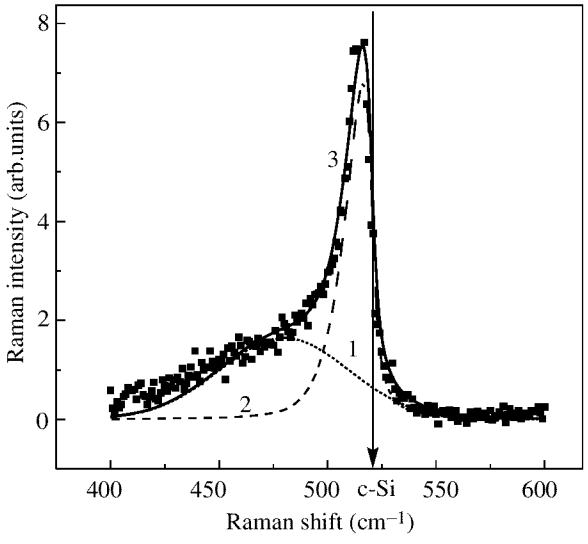

Fig. 1. Raman spectrum of a nanocomposite 'opal-silicon'. 1—'amorphous component' of a spectrum, 2—'nanocrystalline component', 3—'total' spectrum. The phonon frequency corresponding to c-Si is marked.

The Raman measurements were carried out in the backscattering geometry. The spectral resolution was 5 cm^{-1} and the scanning accuracy was about 1 cm^{-1}. The spectra were excited by the 4888 Å line of argon-ion laser.

The samples were filled with platinum to fabricate metal-semiconductor-metal (MSM) junctions. An opal was impregnated with a solution of platinum tetrachloride in ethanol, and then $PtCl_4$ was reduced with hydrogen.

2 Results and discussion

Figure 1 shows the Raman spectrum of an annealed sample. The narrow peak, associated with Raman-active TO phonon mode of crystalline silicon is seen to shift to the low frequency range as compared with a bulk silicon.

Such a transformation of the spectrum testifies to formation of a nanocrystalline phase of silicon [4]. Analysis of Raman spectra within the framework of the model of a strong spatial confinement of optical phonons has allowed to estimate both the average size $L \approx$ 4 nm and volume fraction $\chi = 52\%$ of crystallites in amorphous-nanocrystalline silicon system [5, 6, 7].

TEM study of unannealed sample have shown, that as-deposited silicon film was amorphous with rarely distibuted Si crystallites with sizes about 3–5 nm.

In annealed samples silica spheres are covered uniformly with a 20–25 nm-thick layer of mixed amorphous-nanocrystalline silicon (Fig. 2(a), diffraction contrast mode). The composition was specified by EDX spectrum. Structure state of Si was determined by microdiffraction patterns taken for the large crystals which found to be point patterns with orientation (110).

It is seen (Fig. 2(a)), that Si film on a sphere surface has more dark contrast than sphere itself. The black areas represent the separate grains of nanocrystalline silicon of various

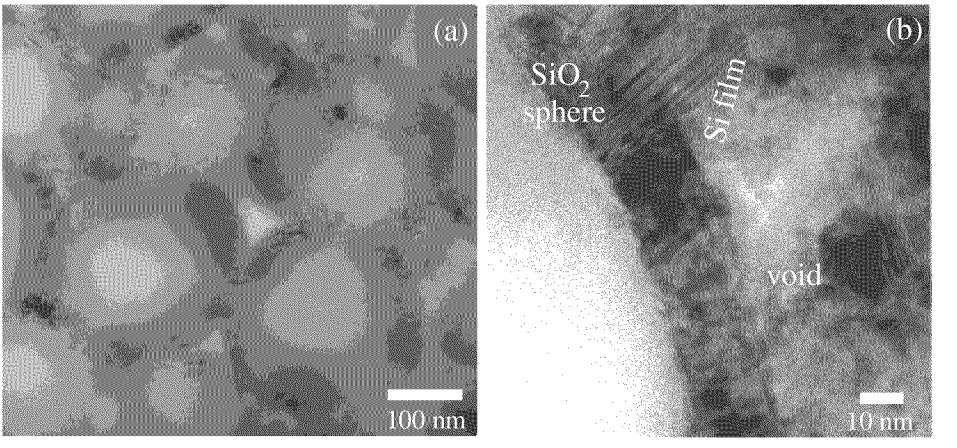

Fig. 2. (a) TEM image of annealed sample 'opal-Si'. (b) HREM image of silicon film on the surface of SiO_2 sphere.

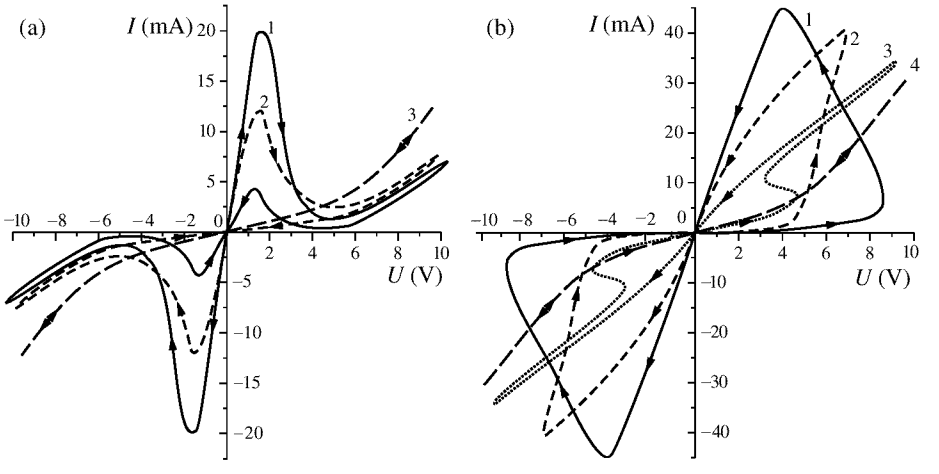

Fig. 3. N-shaped (a) (1—0.1 Hz, 2—100 Hz, 3—10 kHz) and N-S-shaped (b) (1—0.01 Hz, 2—1 Hz, 3—100 Hz, 4—10 kHz) CVC of nanocomposites 'opal-Si-Pt' with different fill factors.

size which are in exact Bragg reflection.

HREM silicon film image (Fig. 2(b)) shows, that the separate grains have single crystal structure over all thickness of the silicon layer. The large grains have hexagon shape. The interface 'Si crystal layer–amorphous silica sphere' is well seen.

In most cases on a silicon film surface there is an amorphous layer, which appears to be silicon dioxide arising as a result of oxidation of the silicon film surface due to surrounding. Its thickness reaches about one thirds of Si film thickness.

The average crystallite sizes are varied from 4 to 10 nm. It is to be noted, that as the thickness of silicon layer exceeds $\approx$ 25 nm and becomes compared with the void size, the cavities in an opal are filled by silicon not completely. Figure 2 illustrates this fact as well.

The empty volume is accessible to fill by other substances. For example, platinum

clusters can be impregnaged into the rest volume. Figure 3(a,b) shows current-voltage characteristics of the nanocomposites 'opal-Si-Pt'. The type of CVC depends on fill factor of Pt. That behaviour of CVC is defined by redistribution of carriers on the Pt-Si interface.

3 Conclusion

It is shown, that the thermal CVD technique allows to deposit the 20–25 nm-thick uniform silicon film on the inner surface of void sublattice of artificial opals. It is established that the thickness of the silicon film and degree of filling can be simple varied by both the duration of the thermal CVD process and the thickness of the opal sample. It, in turn, allows to create 3D multilayer planar structures. 3D arrays of Pt-Si junctions were designed. The structures fabricated is found to have S- or N-like CVC.

Acknowledgements

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